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⑥ INVESTIGATIONS OF THE STRUCTURES AND DYNAMICS  
OF MOLECULES BY ELECTRON DIFFRACTION,

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by

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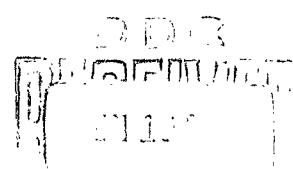
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Contract AF 49(638)-783  
United States Air Force  
Air Force Office of Scientific Research



④ 16

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### INTRODUCTION

This report is a summary of accomplishments under the three-year contract AF 49(638)-783. Because the contract has been extended in the form of a grant (Grant No. AF-AFOSR 281-63) for one year, the present report has purposely been kept short with the intention of submitting a fuller account later. For this reason, wherever possible in the text that follows reference is made to previous reports or the literature in place of review here.

Accomplishments under the contract have been many. Four extensive articles dealing with contract work have appeared in scientific journals, and at this writing three more manuscripts are complete and shortly to be submitted. Some half-dozen structure investigations have been completed and are to be published as soon as manuscripts can be prepared, and some five additional studies are currently in progress. Contract work has been reported on in two international scientific meetings.

Four graduate students have received support under the contract, and their theses will comprise almost entirely the results of contract work. Other personnel have been undergraduate students and two post-doctoral fellows, as well as the principal investigators.

### STRUCTURAL WORK

The contract work may be divided into three categories: 1) substances of unusual structural interest by reason of geometry, 2) vibrational amplitude studies, and 3) methods of structure determination.

In the first category are found the molecules 1) dinitrogen pentoxide ( $N_2O_5$ ), 2) fluorine fluorosulfonate ( $SO_3F_2$ ), 3) cyclopropane ( $C_3H_6$ ),

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In the first category are found the molecules 1) dinitrogen pentoxide ( $N_2O_5$ ), 2) fluorine fluorosulfonate ( $SO_3F_2$ ), 3) cyclopropane ( $C_3H_6$ ),

4) butadiene-1,3 ( $C_4H_6$ ), 5) disiloxane ( $(SiH_3)_2O$ ), 6) hexachlorobenzene ( $C_6Cl_6$ ), and 7) hexabromobenzene ( $C_6Br_6$ ).

Dinitrogen pentoxide has turned out to be a difficult problem in its details. The gross configuration has been determined, almost certainly, to be  $O_2N-O-NO_2$  and the bond distances and bond angles are accurately measured with the single exception of the angle at the central oxygen atom. This oxygen angle depends upon measurement of the  $N \cdots N$  distance, which has a value near that of all other interactions across one bond angle and hence is unresolved from them. Also, the relative orientation of the two  $-NO_2$  groupings is not yet known with certainty: the two groups appear to have rather large rotational motion about the N-O single bond so that the longer distances from one group to the other are nearly "washed out." However, quite good agreement has been obtained with a model in which the average angles of twist of the two  $-NO_2$  groups are  $60^\circ$  and  $150^\circ$  with respect to the plane defined by the bonds at the central oxygen atom. Work is being continued, and a preliminary short communication of our results is contemplated. More details of the work are to be found in Technical Operating Report No. 5.

The structure of fluorine fluorosulfonate has been verified to have bonds directed toward the corners of a distorted tetrahedron from the central sulfur atom. Because the structure has no symmetry and many parameters, it has been possible to measure the several bond distances and bond angles only roughly. We feel that it would be possible to do a better job with better data, but no further work is contemplated. Publication of our current results is planned. Details of this work are found in Technical Operating Report No. 3.

4) butadiene-1,3 ( $C_4H_6$ ), 5) disiloxane ( $(SiH_3)_2O$ ), 6) hexachlorobenzene ( $C_6Cl_6$ ), and 7) hexabromobenzene ( $C_6Br_6$ ).

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The structures of cyclopropane, butadiene-1,3, disiloxane, and the two hexahalobenzenes were refined from data brought from Norway by Professor O. Bastiansen after preliminary work had been done in his laboratory. The results for these molecules are given in Technical Operating Report No. 7. This work is complete, and is being prepared for publication.

The second category of work under the contract has so far included studies of phosphorus trichloride ( $\text{PCl}_3$ ). The essential purpose of these investigations is to learn what use may be made of measurements of amplitudes of vibration for the determination of potential constants or other interesting quantities connected to molecular motions.

The work on phosphorus trichloride has resulted in the first measurement by electron diffraction of the effect of temperature on the structure of a gaseous molecule. These results, together with data from spectroscopy, led to the determination of a general set of quadratic potential constants, the first examples of such a general determination. These results were presented in part at a symposium "Thermal Motions in Molecules and Crystals" held in connection with the 5th International Congress of Crystallography in Cambridge, England, in August, 1960, and again at a symposium on "Electron and Neutron Diffraction" held in Kyoto, Japan, in September, 1961. Publications are listed in the Bibliography as items 1, 2 and 4; reprints of 1 and 2 accompany this report. Details are also given in Technical Operating Report Nos. 3 and 4.

The third category of work has included primarily a detailed study of the method of least squares and its application to the refinement of molecular structures by use of electron-diffraction intensity data. The study has been

extensive, and has led to the development of complicated computer programs which permit an almost automatic refinement of suitable trial structures in times many-fold shorter than may be attained with conventional methods. Publication of this work is expected shortly: three manuscripts have been prepared. Descriptions are found in Technical Operating Report Nos. 2, 3 and 6. In addition to the least squares work, a short method for taking account of the effect of centrifugal distortion on bond distances and bond angles was worked out during the phosphorus trichloride investigations. The publication is listed as item 3 in the Bibliography and a reprint is included in this report.

WORK IN PROGRESS

At termination of the contract period a number of studies were under way and are being carried on as part of the work under the grant-in-extension. These include investigations of cyclooctadiene-1,5 ( $C_8H_{12}$ ) and disilyl sulfide ( $(SiH_3)_2S$ , since finished), both substances of particular structural interest; and nitrogen dioxide ( $NO_2$ ) and arsenic tribromide ( $AsBr_3$ ), both being studied in connection with the vibrational amplitude problem.

The cyclooctadiene-1,5 investigation is a part of a larger study of conjugated organic systems. The molecule has carbon-carbon bond distances about as expected and a slightly longer than normal carbon-hydrogen bond distance. Of special interest, however, are the large C-C-C bond angles: the average value of this angle (there are two types, of course, corresponding to single bond - double bond juncture and single bond - single bond juncture) is very close to  $122^\circ$ , in contrast to a normal value for the average of about

117.5°. It is not yet clear how the angle strain is divided between the two angle types, but if each assumes 50% the values  $\angle \text{C}=\text{C}-\text{C}$  = 130° and  $\angle \text{C}-\text{C}-\text{C}$  = 114° would result. The answer to this question is connected to other structural questions, such as whether the configuration corresponds to "tub" or "chair" form, and if the former, the amount of twist about the 3 and 7 bonds: in the event of a "tub" configuration this twist is undoubtedly present in order to give better steric relationship of the hydrogen atoms. Further description is found in Technical Operating Report No. 9.

The work on disilyl sulfide was undertaken in order to throw further light on the nature of the bonds formed by silicon: in siloxane, the oxygen analogue of disilyl sulfide, the bond angle at oxygen is a surprising 144° (Technical Operating Report No. 7) and in trisilyl amine the molecule has a coplanar heavy atom structure (K. Hedberg, J. Am. Chem. Soc., 77, 6491 (1955) rather than a pyramidal structure such as has its analogue trimethyl amine. Such large angles suggest, in valence bond language, the use of d orbitals by silicon together with an unshared electron pair from the central atom, and the question is raised as to whether central atoms from other than the first row of the periodic table also permit such silicon bonding. The answer is, apparently not: the sulfur angle in disilyl sulfide is entirely normal. The final results for this molecule are

	r, Å°	u, Å
Si - H	1.506	0.109
Si - S	2.134	0.046
Si...S	3.209	0.118
Si...H	2.969	0.217

∠ SiSSi	97.5°
∠ HSiS	108.0°

A manuscript is to be prepared shortly for publication.

The work on nitrogen dioxide is nearing completion. Structural results are presented in Technical Operating Report No. 9. The investigation of the potential constant problem is in progress. The work on arsenic tribromide has just been started. Its purpose is to check the conclusions reached in the earlier, analogous investigation of phosphorus trichloride, and to that end the structure will be studied at two temperatures.

#### PARTICIPANTS IN WORK

The following list is composed of those who have made some direct contribution on a research level, and omits a number of service personnel whose help has been invaluable.

1. Kenneth Hedberg, Principal Investigator
2. Lise Hedberg, Principal Investigator
3. Otto Bastiansen, Visiting Professor and Research Associate
4. Machio Iwasaki, Research Associate
5. David Barnhard, Graduate Student
6. Jerome Blank, Research Assistant
7. Frederick Fritsch, Research Assistant
8. Ellen Gaskell, Research Assistant
9. Celia Rockholt, Research Assistant
10. Robert Ryan, Research Assistant

REPRINTS OF PUBLISHED WORK

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Publications

1. "Effect of Temperature on the Structure of Gaseous Molecules. Structure of  $\text{PCl}_3$  at  $300^\circ$  and  $505^\circ\text{K}$ ." K. Hedberg and M. Iwasaki, J. Chem. Phys. 36, 589 (1962).
2. "Potential Constants of  $\text{PCl}_3$  from Amplitudes of Vibration and Normal Vibration Frequencies," M. Iwasaki and K. Hedberg, *ibid.* 36, 594 (1962).
3. "Centrifugal Distortion of Bond Distances and Bond Angles," M. Iwasaki and K. Hedberg, *ibid.* 36, 2961 (1962).
4. "Effect of Temperature on the Structure of Gaseous Molecules," K. Hedberg and M. Iwasaki, J. Phys. Soc. Japan, 17, Supp. B-II, 32 (1962).

Technical Reports

The manuscripts for the first two articles listed under Publications were submitted separately as Technical Reports. Later information suggested it was advisable to wait for publication.

Technical Operating Reports

"Investigations of the Structures and Dynamics of Molecules by Electron Diffraction," K. Hedberg and L. Hedberg.

No. 1 -- January - March, 1960.  
No. 2 -- April - June, 1960.  
No. 3 -- July - September, 1960.  
No. 4 -- October - December, 1960.  
No. 5 -- January - March, 1961.  
No. 6 -- April - June, 1961.  
No. 7 -- July - December, 1961.  
No. 8 -- January - June, 1962.  
No. 9 -- July - December, 1962.